

STUDIES IN THE THICKNESS OF ADSORBED VAPOR FILMS

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

BY

HARRY EDWARD SMITH

Baltimore

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THE THICKNESS OF ADSORBED VAPOR FILMS

The following experiments are an account of a series of investigations which were carried out with a view of ascertaining the thickness of the adsorbed films on *plane* surfaces. At the present time the phenomena of adsorption are theoretically classified by means of three distinct and unrelated generalizations. The unimolecular layer theory of Langmuir, the multi-molecular layer theory of Eucken-Polyani, and the capillary theory of Zsigmondy. The phenomena are so vague and uncertain that we find all three theories enjoying considerable vogue, each claiming to be applicable to certain experimental conditions. The uncertainty and modesty of the various proponents of the above theories is largely due to the difficulty of interpreting the various experimental results on the basis of any one theory. For example we find that Langmuir¹, and Carver² experimentally prove that the adsorbed layer is unimolecular in thickness. On the other hand Warburg and Ihmori³, Pettijohn⁴, Briggs⁵, D'Huart and Hackspill⁶, and McHaffie and Lenher⁷ submit equally conclusive experimental evidence that shows that the adsorbed film is multi-molecular in thickness on plane surfaces. This disagreement is not however considered serious by reason of the fact that the experimental conditions were not the same in the above experiments. It is generally believed that the unimolecular adsorbed film is to be found under low equilibrium pressures or at temperatures high above the critical temperature. On the other hand it is thought that the multimolecular layer is formed at pressures close to the saturation pressure. However the two phenomena are by no means clearly defined and there remains a chaotic condition as far as the quantitative aspect of the question is concerned.

Patrick⁸ has for years held the opinion that the capillary theory is the most promising for explaining the phenomena of adsorption of vapors by porous bodies. It was also clearly recognized that the classical theory of capillarity was inadequate to account for the experimental adsorption results. Experiments were accordingly inaugurated in this laboratory to test the validity of the Lord Kelvin relation that governs the relation between the vapor pressure of a liquid and its radius of curvature. The results of these experiments (unpublished) were so encouraging that our belief in a modified capillary theory of adsorption was greatly strengthened. The acceptance of

¹ Langmuir: J. Am. Chem. Soc., **38**, 2221 (1916); **40**, 1361 (1918).

² Carver: J. Am. Chem. Soc., **45**, 63 (1923).

³ Warburg and Ihmori: Wied. Ann., **31**, 1006 (1887).

⁴ Pettijohn: J. Am. Chem. Soc., **41**, 477 (1919).

⁵ Briggs: J. Phys. Chem., **9**, 617 (1905).

⁶ D'Huart and Hackspill: Compt. rend., **180**, 1581 (1925).

⁷ McHaffie and Lenher: J. Chem. Soc., **127**, 1559 (1925); **1926**, 1785; Lenher: **1927**, 272.

⁸ Patrick: Colloid Z. **36**, Zsigmondy Fest., 272 (1926).

such a theory however placed us in direct opposition to the multimolecular theory of Eucken-Polyani. In other words we were forced to choose between the capillary or the multimolecular theories of adsorption. Such a position led to a careful examination of the experimental proofs of the existence of an adsorbed film of multimolecular dimensions.

Practically all of the evidence proving the existence of multimolecular adsorbed films was based on experiments made on glass. This material while admirably suitable for obtaining optically plane surfaces seemed to us to offer the possibility of easily being roughened from the standpoint of molecular dimensions. Glass is not a chemically inert substance, it being admittedly attacked by water and acids. The results of such action must be the elimination of alkali and the deposition on the surface of amorphous silica. It therefore seemed plausible to seriously question the results of all adsorption measurements made on acid-cleaned glass surfaces in so far as the results were interpreted from the standpoint of molecularly plane surfaces.

While it is true that most of the measurements were made on glass surfaces, a number of other surfaces were also employed, such as mica, platinum, and quartz. The present paper does not deal experimentally with any of the latter surfaces; but it is pertinent to the discussion that follows to point out the possibility of all of these surfaces being not plane from the molecular dimensions standpoint. Mica surely exhibits capillary spaces between its lamellae, platinum is roughened by alternate heating and cooling (the so-called "activation" of its surface). Furthermore highly polished platinum in X-ray diffraction studies no longer shows the characteristic platinum lines, but exhibits the structure of an amorphous substance. Quartz when heated to the melting point is known to sublime, which fact may easily account for the failure to obtain molecularly plane surfaces with this material.

We were led to believe that a supercooled liquid offered the best possibility of securing a plane surface. The surface energy of the liquid would insure a minimum surface, and if care were exercised to prevent corrosion of this surface after cooling it should be plane.

The adsorption measurements were made according to the method of McHaffie and Lenher, this being considered as offering the fewest experimental difficulties.

The method employed by McHaffie and Lenher in studying the thickness of adsorbed films was to measure the vapor pressure in a vessel of known volume and surface area throughout a temperature range sufficient to insure the existence at the lower temperature of liquid and at the higher temperature of all the vapor in the gaseous condition. When no adsorption of the vapor on the walls of the vessel took place, the P. T. diagram would appear as in Fig. 1, curve A, O, C.

The straight line (CB, O) represents the ordinary thermal increase of gaseous pressure with increasing temperature, while the lower curve (A, O) is the vapor pressure curve of the condensed vapor. If however the vapor is appreciably adsorbed the curve (B, C) will no longer intersect the vapor pressure curve (A, O) at the point (O) but will follow a course as shown by

the dotted line. It is further evident that one may calculate the total number of molecules of water vapor present at the point O, this number should remain constant at all temperatures above T° , i.e. above the dew point. It is obvious however that the total number of molecules has decreased at points along the dotted curve and that this decrease may be simply calculated and thus the number of molecules adsorbed be ascertained.

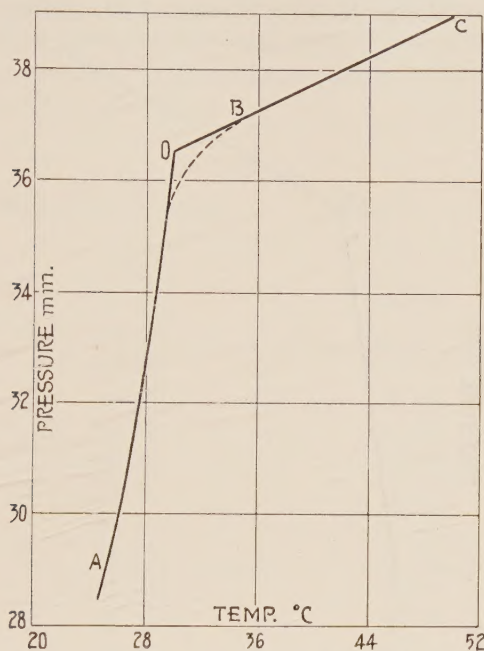


FIG. 1

As stated above the results of McHaffie and Lenher showed marked adsorption i.e. marked deviation from the ideal P. T. curve (I). In fact the thickness of the adsorbed water film on glass was found to be of the order of a hundred molecules, on platinum, and quartz thinner layers were found, but still decidedly multimolecular in thickness.

The weak point in the work was the assumption that glass cleaned with chromic and nitric acids still presents a plane surface. The writer was strongly of the opinion that such a cleaning dissolved out some of the alkali from the glass, leaving a roughened surface of unknown extent, and in addition left the silica in an amorphous state which is most suitably adapted for the adsorption of vapors. We therefore determined to repeat these measurements taking special precautions to obtain a truly plane surface. At this point it may be of interest to make a rough calculation of the amount of amorphous silica that would be sufficient to account for the total adsorption in the case of toluene. Subsequent results will show that the maximum adsorption of toluene at the saturation pressure amounted to .000075 gm., to

adsorb this amount of toluene only .2 mgm. of silica gel is required. It is therefore entirely probable that by the action of strong acids on glass this small amount of amorphous silica may well be produced. From this calculation it is evident that it is impossible to believe that the surface of acid-washed glass presents a plane surface. However a freshly molten glass surface that had come in contact only with dry air should present a truly plane surface from the standpoint of adsorption measurements. Accordingly a glass bulb was blown, the glass blower blowing through P_2O_5 during the operation.

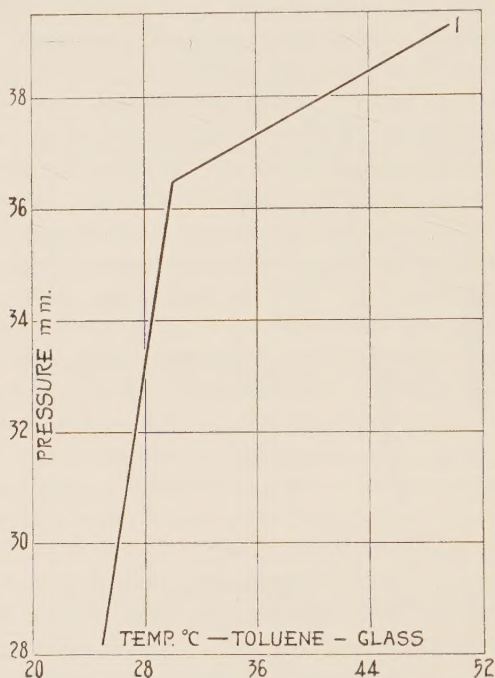


FIG. 2

Furthermore in order to avoid any possible solvent action of water upon the glass surface it was decided to study the adsorption of toluene.

While it is true that McHaffie and Lenher obtained adsorption when working with water vapor on quartz and platinum surfaces, it is significant that the "thickness" of the layers on these surfaces was much less than on etched glass. The quartz was washed with acid and it is highly probable that a roughening took place during the operation. Platinum is known to be activated by heating in air, this we believe is due to the formation of finely divided platinum on its surface.

The apparatus is essentially the same as that employed by McHaffie and Lenher. The temperatures were carefully measured and the pressures read with a cathetometer to within .03 mm. The results obtained with toluene vapor on a virgin glass surface are given in Tables I and II and these same data are graphically shown in Curves (2) and (1). It can be immediately seen that toluene vapor shows no adsorption at any temperature. It is to be

noted that the method is not sufficiently sensitive to ascertain the presence of a unimolecular layer. Such a layer may be and undoubtedly is present at all temperatures. But we may definitely draw the most important conclusion from this experiment, that a multi-molecular layer film of toluene cannot exist on a plane surface.

In order to further prove our contention that a glass surface treated with cleaning solution and with nitric acid is no longer plane, we cleaned a bulb with the above acids, washed and thoroughly dried the surface. This bulb was then sealed to our apparatus and another series of P. T. measurements made with toluene vapor. The results are tabulated in Table III and graphically shown in Curve (3) Fig. 2.

TABLE I
Virgin Glass Surface. Toluene.

T °C.	P Mm.	T °C.	P Mm.
50.00	39.25	30.80	36.60
47.00	38.90	31.00	36.60
45.00	38.65	30.00	36.30
43.50	38.40	29.71	35.70
40.00	37.90	29.40	35.30
37.00	37.65	29.20	34.90
35.00	37.35	29.00	34.50
33.00	36.95	28.00	32.85
30.07	36.45	27.04	31.25
30.60	36.55	26.00	29.80
30.40	36.55	25.06	28.15
30.20	36.50	25.80	29.35

TABLE II
Virgin Glass Surface. Toluene.

T °C.	P Mm.	T °C.	P Mm.
50.00	30.95	26.04	28.65
47.00	30.70	25.80	28.60
45.00	30.60	25.60	28.55
40.00	30.00	25.45	28.55
43.00	30.35	25.20	28.20
37.10	29.70	25.00	28.00
35.00	29.55	24.80	27.65
33.00	29.35	24.40	27.15
31.00	29.20	24.00	26.70
30.04	29.05	23.00	25.20
29.00	28.95	22.00	23.85
28.07	28.85	21.00	22.65
27.07	28.75	20.00	21.60

TABLE III

Acid-treated Glass Surface.		Toluene.	
T °C.	P Mm.	T °C.	P Mm.
50.00	30.40	28.80	28.23
47.05	30.10	29.15	28.30
43.50	29.85	27.81	28.10
40.00	29.45	27.00	27.93
38.00	29.25	26.00	27.75
35.10	29.00	25.00	27.55
33.12	28.75	24.60	27.20
32.20	28.60	23.20	25.80
30.00	28.35	22.20	24.25

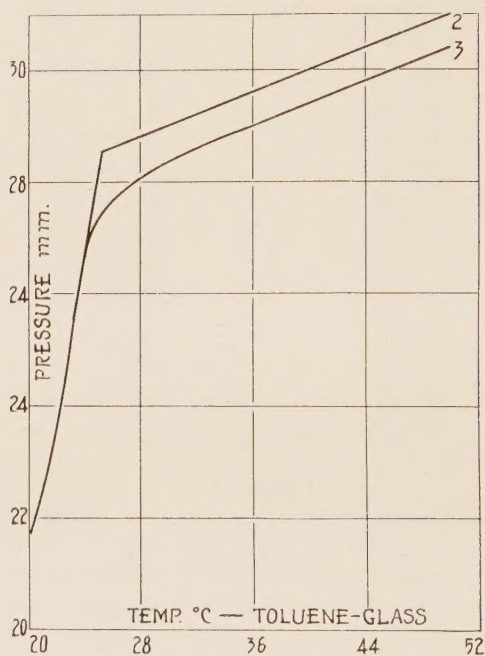


FIG. 3

It is to be noted that in the case of the acid-washed surface very different results were obtained from those on the virgin glass surface. In the former case we duplicated the experiments of McHaffie and Lenher made with water vapor. There is a decided rounding of the flex point of the curve which undoubtedly is due to the removal of the toluene from the vapor phase before the condensation temperature is reached. In other words adsorption of the toluene vapor occurs on the glass surface. But it is surely absurd to attempt to calculate the thickness of this adsorbed layer, for we have absolutely no information regarding the extent of the surface. This adsorption undoubtedly

owes its origin to the capillary condensation of the toluene vapor in the amorphous silica produced by the action of water and acid on the glass surface.

Experiments were also carried out with water vapor on virgin glass surfaces. The results of such measurements are given in Tables IV-VI and curves (4, 5, 6), Fig. 3.

TABLE IV

Virgin Glass Surface.		Water.	
T °C.	P Mm.	T °C.	P Mm.
50.00	24.00	30.00	22.00
47.00	23.70	29.90	21.90
45.00	23.50	29.70	21.70
43.00	23.35	29.50	21.55
40.00	23.05	29.00	21.35
37.00	22.75	28.00	20.65
35.00	22.50	27.50	20.50
33.15	22.35	26.00	19.85
32.50	22.25	25.00	19.20
31.00	22.10		

TABLE V

Water-etched Glass Surface.		Water.	
T °C.	P Mm.	T °C.	P Mm.
25.09	19.10	31.40	21.75
26.00	19.55	32.37	21.90
27.00	19.85	33.88	22.20
28.14	20.25	35.00	22.25
28.70	20.70	37.00	22.45
29.00	21.05	40.00	22.70
29.50	21.30	42.90	23.05
29.74	21.40	45.00	23.20
30.00	21.35	50.00	23.55
30.49	21.55		

TABLE VI

Water-etched Glass Surface.		Water.	
T °C.	P Mm.	T °C.	P Mm.
25.07	18.70	30.44	20.70
27.10	19.25	32.03	20.95
28.04	19.70	35.07	21.45
29.10	20.00	38.40	22.10
29.42	20.25	42.65	22.60
29.90	20.45	45.00	22.80

A number of interesting points in connection with these experiments are to be noted. In curve (4) Fig. 3, which represents measurements made with water vapor on a virgin glass surface, care being exercised that in the filling of the bulb with vapor no condensation was allowed to take place. Apparently these results show no adsorption of the water vapor. However the intersection of the two curves does not occur on the vapor pressure curve of water, i.e. the lower portion of the curve indicates a decided lowering of the water pressure. Such a result would be expected if the water dissolved some of the soluble constituents of the glass, such as sodium hydroxide. Curve (5)

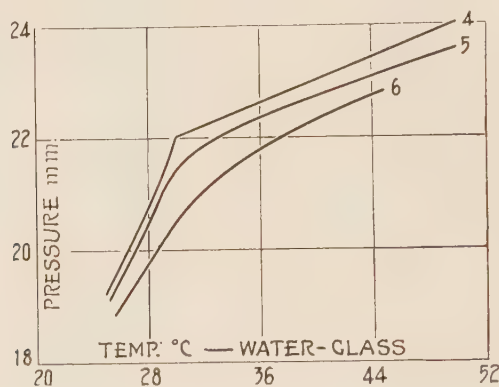


FIG. 4

and Table V show the results obtained when measurements were taken in the reverse direction, i.e. when the temperatures were increased and the corresponding pressures measured. Here we have marked evidence of "adsorption" having taken place. But inasmuch as we do not know how much the vapor pressure is reduced by the solutes present, or by the capillary action of the amorphous silica, it is absurd to attempt a calculation as to molecular thickness of the adsorbed film, etc. Curve (6) and Table VI show that as time goes on the solvent action of the water vapor on the glass increases i.e. there is now a most marked divergence of the P. T. curve from the ideal case where no adsorption takes place. At this point it is interesting to note that a fresh glass bulb was filled with water vapor and allowed to stand for four months. At the end of this time only a vapor pressure curve was obtained on making the P. T. measurements. This indicated that the action proceeded until a saturated solution was present on the glass surface.

Of course these observations are extreme, due to the fact that a fresh glass surface was employed. Practically all investigators when dealing with glass have washed the surface either with water or with acids. This of course tends to remove the soluble alkali, leaving the residue of amorphous silica nevertheless.

In order to further verify our conclusions regarding the action of water on fresh glass surfaces, we added a few cc. of water to one of our freshly blown

bulbs together with phenolphthalein as an indicator. A distinct alkaline reaction was obtained, in fact we were able to titrate with dilute acid and thus roughly ascertain the amount of alkali dissolved from the glass.

The importance of the above work is truly great provided we are justified in drawing general conclusions from the toluene experiments. There is little information regarding adsorption phenomena that can be gained from the water experiments. We have shown that water vapor attacks fresh glass surfaces in a manner sufficient to destroy the planeness of the surface and thus render all adsorption measurements on such surfaces vague and meaningless. In the case of toluene vapor however there is evidently no action on the glass, the surface remains plane, and important conclusions regarding the thickness of the adsorbed film may be drawn. Whether or not the results obtained with toluene are equally true with other vapors on other plane surfaces is impossible at present to say. We are planning to investigate the adsorption of vapors of polar compounds on plane glass surfaces, and also to attempt to obtain a plane surface which will permit the measurement of the adsorption of water vapor.

If such studies verify our present belief, namely, that the adsorbed vapor film is unimolecular in thickness even at the saturation pressure, then a most important step in the theory of adsorption will have been taken. Such an experimentally proven fact would immediately render untenable the theories of adsorption proposed by Eucken and Polyani. The very essence of such theories is that the adsorbed layer is multimolecular in thickness and they must necessarily be abandoned if it can be proven that the layer is never greater than unimolecular in thickness on a plane surface.

There remain the Langmuirian theory for plane surfaces, and the capillary theory to account for the adsorption by highly porous bodies.

Summary

1. It has been shown that the thickness of the adsorbed film of toluene on a plane surface is never greater than unimolecular, even at saturation pressures.

2. Glass washed with acids and water does not present a plane surface.

3. Water vapor reacts with fresh glass surfaces so as to render the latter no longer plane.

4. The significance of the above experiments was briefly discussed in relation to their bearing on the existing theories of adsorption.

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BIOGRAPHY

The author of this dissertation, Harry Edward Smith, was born March 1, 1902 at Bowie, Maryland. He received his early education in the public schools of Maryland. He was graduated from the Baltimore Polytechnic Institute in 1921. He received the degree of B. S. in Chemistry from the Johns Hopkins University in 1924, and began the graduate study of chemistry in the fall of the same year. He has been in attendance there continuously since that time. He held Hopkins Scholarships during the years 1924-1925 and 1925-1926 and a University Scholarship in 1926-1927.

